Stability of Detached-Grown Germanium Single Crystals

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Introduction

During detached Bridgman growth, the melt meniscus at the tri-junction (gas-liquid-solid) is not in contact with the wall of the ampoule. This phenomenon, which is also called dewetting or necking, has been observed in recent years, mainly in microgravity experiments. Reviews about this growth-techinque, are given e.g. by Regel and Wilcox et al. [1] and Duffar et al. [2]. Under Earth conditions, it is more difficult to achieve detached Bridgman growth, because of the hydrostatic pressure, which counteracts the detachment mechanism.

Main factors and parameters promoting detachment:

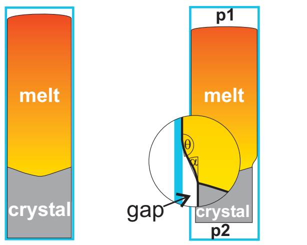
- **high contact angle θ between the crucible material and the melt**
  for germanium on a pBN substrate, a contact angle around 170° was measured [3]
- **high growth angle α**
  the growth angle for germanium is 7-13° [4]
- **pressure difference Δp between the melt meniscus and the top of the melt**
  pressure difference is possible through the use of the closed-bottom pBN container

Sufficient condition for detachment [2, 5]:

$$\alpha + \theta \geq 180°$$

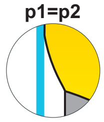
α: growth angle; θ:wetting angle

Bridgman growth **Detached Bridgman**



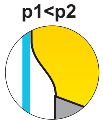
Influence of additional pressure below the meniscus

p1=p2



The pressure above the melt (p1) and below the meniscus (p2) are the same. This is the case in the open-bottom pBN tube (compare the ampoule configuration on the upper right). Detachment can only occur if $\alpha + \theta \geq 180°$.

p1<p2



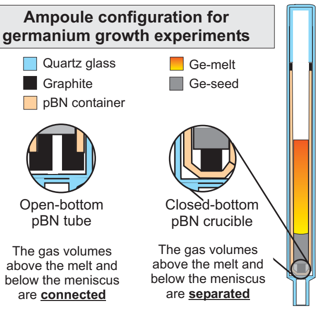
The pressure above the melt (p1) is lower than the pressure below the meniscus (p2). This promotes the detachment and can be achieved with the closed-bottom pBN crucible.

Experimental Setup

Germanium
- (111)-orientation, Ga doped ($7 \cdot 10^{18}$ at/cm^3)
- (110)-orientation, undoped
- grown length: 45 - 60mm
- diameter: 12mm

Furnaces
- Multizone Furnace UMC (24-zones)
  translation-free, zone programming
  axial temperature gradient: 20-30K/cm
- 7-zone vacuum furnace
  with translation mechanism (5mm/h)
  axial temperature gradient: 25-35K/cm

Ampoule configuration for germanium growth experiments

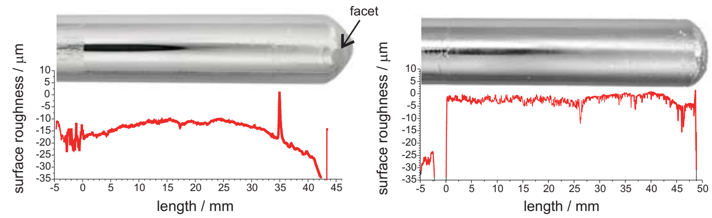


The gas volumes above the melt and below the meniscus are **connected**

The gas volumes above the melt and below the meniscus are **separated**

Detached grown germanium crystal
grown in closed-bottom crucible

Attached grown germanium crystal
grown in open-bottom tube



Micrographs from the surface

Fig.1 (above): All experiments performed in closed-bottom pBN crucibles resulted in single crystals that were mostly detached. One completely detached-grown crystal is shown together with an axial profilometer scan in the figure above. Three growth lines in the (111)-oriented crystal along the axial direction are an indication of single crystallinity (note also the facet at the top of the crystal). The average gap thickness in this crystal is 15µm. A contributing factor to the detachment in the closed-bottom configuration is a higher gas pressure below the meniscus compared to the pressure above the melt. This pressure difference might either be established by shrinking the gas volume around the seed at the beginning of the experiment, by the rejection of volatile impurities [6], or by a combination of both. For a reference condition, attached crystals were grown in open-bottom tubes. In addition to the profilometer measurements, the surface roughness was investigated by electron and optical microscopy.

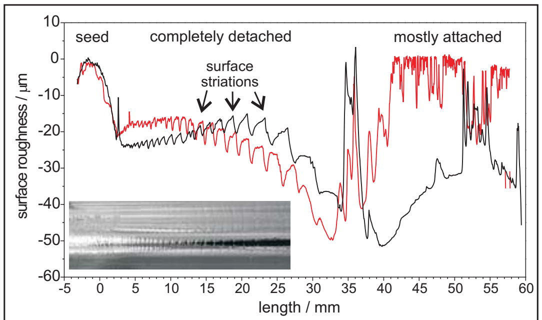
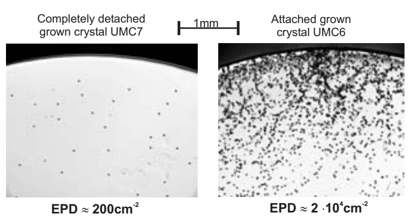


Fig.2: Two axial profilometer scans, performed with an azimuthal distance of 180°, are shown together with a micrograph from crystal VF8, grown in a closed-bottom ampoule. Strong surface striations with a fluctuation of the gap thickness up to 7-8µm are observed. After the growth length reached 35mm, the crystal attached to the wall.
The reason of the instability during detachment is explained with the figure below.

Etch Pit Density



EPD ≈ 200cm^{-2} EPD ≈ $2 \cdot 10^4$cm^{-2}

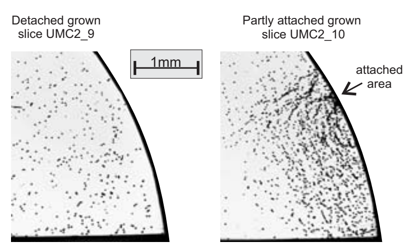
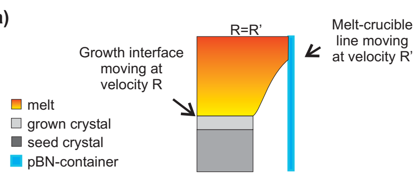


Fig.4: Etched radial wafers to reveal the etch pit density.
Top: In the detached-grown sample the EPD is reduced by two orders of magnitude compared to the attached sample.
Bottom: After a localized attachment the EPD increases rapidly.

a)



b)

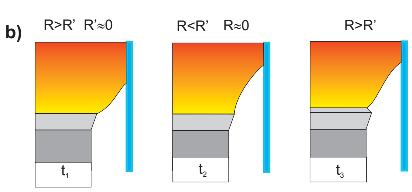


Fig.3: We assume different translation rates of the **crucible**-melt-gas tri-junction (translation rate R') and of the **crystal**-melt-gas tri-junction (translation rate R). Only if the two velocities are equal, will the meniscus shape, and the crystal diameter remain constant during growth (fig.3a). If the translation rates are different, the meniscus shape will get out of equilibrium with respect to the growth angle. As a result of this disequilibrium the meniscus starts to put some force onto the melt crucible line. This force tends to restore the shape of the meniscus when R' increases to a value larger than R for a period of time. In fig.3b a growth sequence (t_1, t_2, t_3) during an instability of the meniscus is shown.

Conclusions:

- Single germanium crystals were grown reproducibly
  - detached in closed-bottom pBN containers
  - attached in open-bottom pBN tubes
- In the detached-grown sample, the EPD is reduced by two orders of magnitude compared to the attached one.
- No additional active pressure control was necessary for the detachment
- Typical gap thickness between the crystal and the ampoule wall is around 20µm
- Surface roughness and gap thickness was measured and investigated with profilometer and with optical and electron microscopy
- Strong surface striations on a detached-grown sample can be explained by a kind of stiction of the melt/crucible/gas tri-junction which causes a variation of the meniscus shape and thus, a change in the sample diameter

Literature:

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